selectivity among the monovalent cations. The permeability ratios with respect to sodium were found to be in the following order $H^+(150) > NH_4^+(8.9) > Cs^+(5.8) > Rb^+(5.5) > K^+(3.9) > Na^+(1.0) > Li^+ (0.33)$. The channel is impermeable to anions and to divalent cations and it exhibits saturation and maxima in conductance as a function of ion concentration, voltage dependence of single channel currents, ion competition and block, and concentration dependence of permeability ratios. These conductance properties make the Gramicidin-A channel in some respects similar to the Na^+ and K^+ transmembrane channels responsible for the excitability of nerve and muscle cells; this enhances the interest in the Gramicidin channel.

The Gramicidin-A channel seems to have two binding sites for monovalent cations, as suggested by NMR experiments using ^{13}C marked Gramicidin molecules [2]. The free energy profile for the transport of Na^+ has also been determined [3].

A number of possible structural models for the Gramicidin channel have been considered [4] involving single helices [5, 6], or double helices [4, 7]. In Urry's model, which seems in agreement with a number of experimental works, two left-handed $\beta_{3,3}^{6;3}$ Gramicidin helices are held together at their N-termini (heads) by hydrogen bonding to form a channel with a length of 26 Å and a pore diameter of 4 Å.

A qualitative mechanism of ion transport and ion selectivity has been proposed [8], arising from the liberation of the carbonyl oxygen into the channel, lining it with negative charges. The general picture of the phenomenon, however, is far from complete. Indeed, other molecular conformations could contribute to the conduction process [4] and even small variations in the conformation of the Gramicidin channel could affect the energetics of channel–ion interactions [1].

In order to help our understanding at the molecular level of some of the above problems concerning the interaction between the Gramicidin-A channel and ions and the role played by water in the ion transport process, we have undertaken computer simulation experiments on this system, assuming Urry's model for the channel. As for similarly large systems previously investigated [9, 10], our initial effort has been directed to the evaluation of pair potentials for the interactions between atoms of the residues and of the backbone, and sodium ion/water molecule. This step, which makes possible Monte Carlo and molecular dynamics simulations, required about one thousand three hundred *ab initio* computations even considering the Na^+ ion only. In addition, more than four hundred *ab initio* computations have been carried out to evaluate pair potentials relative to the interaction between Na^+/water molecule and the phospholipid lysophosphatidylethanolamine, which is used to simulate the membrane moiety of the system. Results of Monte Carlo simulations based on the above models and pair potentials are presented [11].

1 D. W. Urry, C. M. Venkatachalam, K. U. Prasad, R. J. Bradley, G. Parenti-Castelli and G. Lenaz, *Int. J. Quan. Chem.: Quantum Biology Symposium, 8,* 385 (1981).
2 D. W. Urry, K. U. Prasad and T. L. Trapane, *Proc. Natl. Acad. Sci. USA, 79,* 390 (1982).
3 D. W. Urry, C. M. Venkatachalam, A. Spisni, R. J. Bradley and K. U. Prasad, *J. Membrane Biol., 55,* 29 (1980).
4 Y. A. Ovchinnikov and V. T. Ivanov, in 'Conformation in Biology', R. Srinivasan and R. S. Sarma (eds.), Adenine Press, New York, 1983, pp. 155–174.
5 G. N. Ramachandran and R. Chandrasekaran, in 'Progress in Peptide Research', Vol. 2, S. Lande (ed.), Gordon and Breach, New York, 1972, pp. 195–215.
6 D. W. Urry, *Proc. Natl. Acad. Sci. USA, 68,* 672 (1971).
7 W. R. Veatch, E. T. Fossel and E. R. Blout, *Biochemistry, 13,* 5249 (1974).
8 D. W. Urry, in *Conformation of Biological Molecules and Polymers, The Jerusalem Symposia on Quantum Chemistry and Biochemistry,* Vol. 5, E. D. Bergmann and B. Pullman (eds.), Israel Academy of Sciences, Jerusalem, 1973, pp. 723–736.
9 E. Clementi and G. Corongiu, *Biopolymers, 21,* 763 (1982).
10 G. Corongiu, S. L. Fornili and E. Clementi, to be published.
11 S. L. Fornili, D. Vercauteren and E. Clementi, to be published.

F3

Molecular Dynamics Simulations of Aqueous Electrolyte Solutions

K. HEINZINGER

Max-Planck-Institut für Chemie, Mainz, F.R.G.

Structural and dynamic properties of various aqueous electrolyte solutions have been calculated from MD simulations where the ST2 and the Central Force model of water were employed [1].

The structural properties of the solutions are discussed on the basis of radial distribution functions, the orientation of the water molecules and their geometrical arrangement in the hydration shells of the ions. An example of the latter case is given in Fig. 1 for a $MgCl_2$ solution [2]. The figure shows that the oxygen atoms of the six water molecules in the first hydration shell of Mg^{++} are positioned at the corners of a regular octahedron, while for Cl^- an octahedral arrangement only is indicated. The four nearest neighbor water molecules around a central one show a tetrahedral structure and the distributions are sharper in the hydrogen atom directions than in the lone pair directions.

Dynamic properties of the solutions such as self-diffusion and rotational diffusion coefficients, reorientation times of the dipole moment vector and residence time of the water molecules in the hydra-

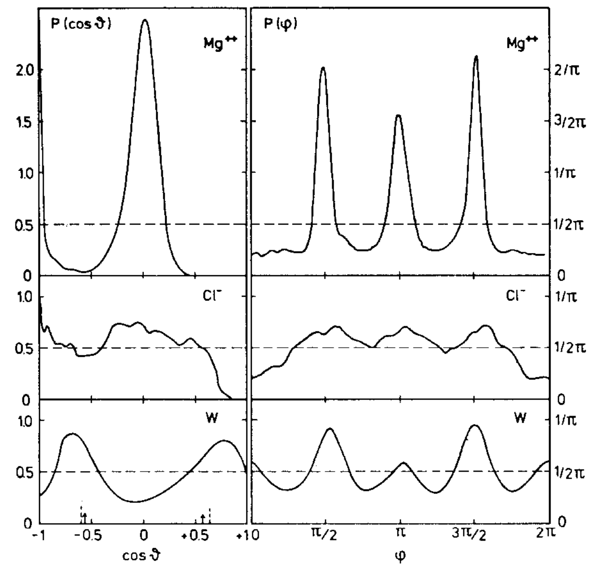

Fig. 1. Probability densities for the polar angle and the azimuth angle of the oxygen atom positions of the six nearest neighbor water molecules around an Mg^{++} and a Cl^- and for the four nearest neighbor water molecules around a central one. The dashed lines indicate uniform distributions.

tion shells of the ions are calculated from the simulation through autocorrelation functions and are compared with experimental results. The spectral densities of the hindered translational and librational motions result from Fourier transformation of the corresponding autocorrelation functions. The dynamic properties can be calculated separately for the water subsystems — hydration water of the cations, the anions and bulk water — and thus provide the possibility of understanding measured macroscopic properties of solutions on a molecular level. The self-diffusion coefficients for the three kinds of water in a LiI solution are given in Table I as an example [3].

TABLE I. Self-diffusion Coefficients for Bulk Water (D^b), Hydration Water of Li^+ (D^+) and of I^- (D^-) in Units of 10^{-5} cm^2/s from an MD Simulation of a 2.2 Molal LiI Solution at 305 °K. D^0 denotes pure water.

i	D^i	D^i/D^0
b	2.85 ± 0.08	0.84
+	1.33 ± 0.10	0.39
−	2.67 ± 0.10	0.78

1 F. H. Stillinger and A. Rahman, *J. Chem. Phys., 60,* 1545 (1974); *68,* 666 (1978).
2 G. Pálinkás, T. Radnai, W. Dietz, Gy. I. Szász and K. Heinzinger, *Z. Naturforsch., 37a,* 1049 (1982).
3 Gy. I. Szász, K. Heinzinger and W. O. Riede, *Ber. Bunsenges. Phys. Chem., 85,* 1056 (1981).

F4

Metal Ion Influence on Hydrogen Bonds in Solvent and Ligands

BERND-MICHAEL RODE

Institute for Inorganic and Analytical Chemistry, Faculty of Science, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

The application of quantum chemical calculations of the all-electron *ab initio* type to studies of metal influence on neighbouring hydrogen bonds has been extended successively to new and larger model compounds during the past decade. Starting with comparatively small systems accessible to fair methodical accuracy due to the use of larger basis sets, some principal effects have been revealed, such as bond contraction, net bond stabilization, charge transfer effects and the increase of rotational barriers around the hydrogen bond [1, 2]. At the same time, such investigations have proved once more the need for the use of *ab initio* type calculations and the incapability of semiempirical procedures for the treatment of metal–solvent or metal–ligand interactions.

The consideration of slightly larger systems such as *e.g.* ion/water/formamide [3] has shown that the effect of the metal ion extends over a long series of bonds, which implies a need for comparatively large 'subunits' of the molecular (or rather 'supermolecular') system for a conclusive quantum theoretical study. This fact was also revealed by the quantum chemically predicted electronic rearrangements taking place in complexes with more than one ligand with the ability to form chelate structures [4]. For this reason, the applicability of minimal basis sets, allowing an extension of the supermolecular model system to considerably larger subunits, had to be tested. The conclusions of such tests [2, 3] have shown that such basis sets can be used for the evaluation of intermolecular geometrical parameters and relative energy effects, still maintaining sufficient accuracy, especially if basis set error corrections like the counterpoise procedure [5] are employed.

The data of *ab initio* calculations for ion/ligand interaction form the basis of three main approaches to more complex systems:

(1) The evaluation of pair and three-body potentials, representing the basis for the construction of interaction potentials used in methods like Monte Carlo or Molecular Dynamics calculations on large ensembles of ions and molecules and/or macromolecules [*e.g.* 6–8].

(2) The 'static' treatment of large supermolecular species with small basis sets for the evaluation of geometries, binding energies, electron density distribution and other data for solvated ions or ion/ligand complexes.